Naturally Occurring Arsenic In Well Water in Wisconsin

By Tom Riewe, Annette Weissbach, Liz Heinen, and Rick Stoll

Naturally occurring arsenic has been found in the ground water of almost every aquifer of Wisconsin, extending through the entire geologic column (Figure 1). However, arsenic contamination is especially prevalent in some of the sedimentary bedrock formations of northeastern Wisconsin. In this part of the state, approximately one-third of the private drinking water wells in Outagamie and Winnebago counties have arsenic detects exceeding a concentration of 5 parts per billion (ppb) (Figure 2). Water sample results indicate about 3.5 percent of these wells have concentrations exceeding the current public drinking water standard of 50 ppb. Concentrations detected in several existing wells in this region are in the thousands of ppb and represent some of the highest found naturally occurring in the world. A sample from one well had a concentration of more than 15,000 ppb.

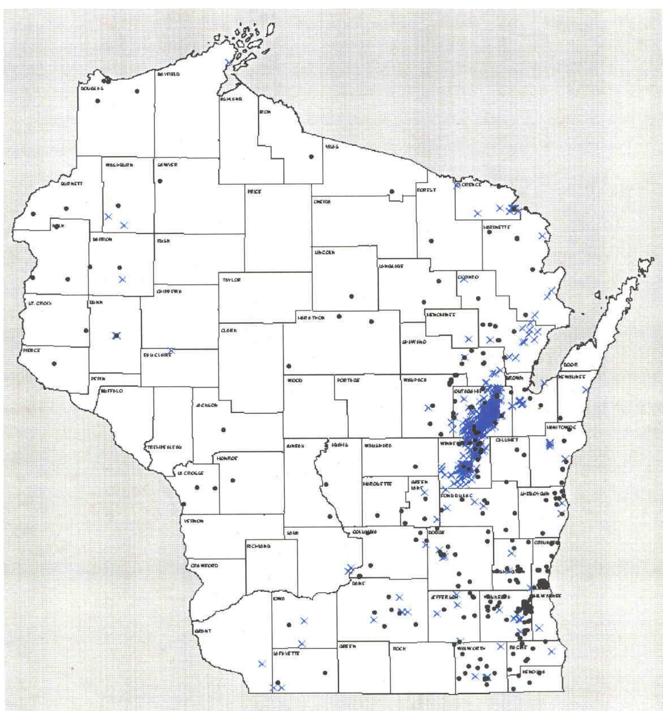

Figure 1. Location of wells with detects of arsenic exceeding 5 parts per billion (ppb). Private Wells shown by check marks, public wells by dots. (Map by Ann Schachte)

New wells constructed to meet more stringent specifications recommended by the Wisconsin Department of Natural Resources (DNR) will, in most cases, produce water with significantly lower concentrations of arsenic. These specifications include deeper casing settings and grouting requirements. However, a small percentage of wells constructed to these specifications have recently been producing water with increasing concentrations of arsenic. This has cast some doubt on the ability of these specifications to provide a long-term solution to the problem.

Furthermore, as a public health issue, the arsenic contamination problem is likely to become more difficult to deal with in the near future. This is because the U.S. Environmental Protection Agency (EPA) has recently proposed lowering the drinking water standard for arsenic in water supplied by public water systems. Their proposal is based on results of ongoing risk assessment studies that have shown arsenic to pose a more serious health concern than previously thought. The EPA will most likely set the new standard somewhere between 3 and 10 ppb.

The DNR expects the EPA to make a decision regarding the revision of the standard in 2000. The final rule is due in January 2001.

The original standard of 50 ppb was set in 1946 by the National Board of Health. In 1977 the EPA adopted this as an interim standard, and later converted it into a primary drinking water standard. For comparison, the World Health Organization has established a provisional standard of 10 ppb for arsenic. (One small drop from an eyedropper in an Olympic-size swimming pool represents about 1 ppb.).

If the EPA sets the new arsenic standard at 5 ppb, water from as many as 30,000 private wells in northeastern Wisconsin could exceed it. Furthermore, based on sample results from public water systems, if the EPA sets the standard at 5 ppb, more than 300 wells serving public water systems throughout Wisconsin could exceed the standard. (This number includes nontransient, noncommunity water systems.) More than 100 of these public wells serve municipal water systems. If the standard is lowered to 2 ppb, more than 750 wells serving public water systems could exceed the standard. More than 250 of these serve municipal systems. To put this into perspective, roughly 17 percent of all municipal wells in Wisconsin could exceed an arsenic standard of 2 ppb.

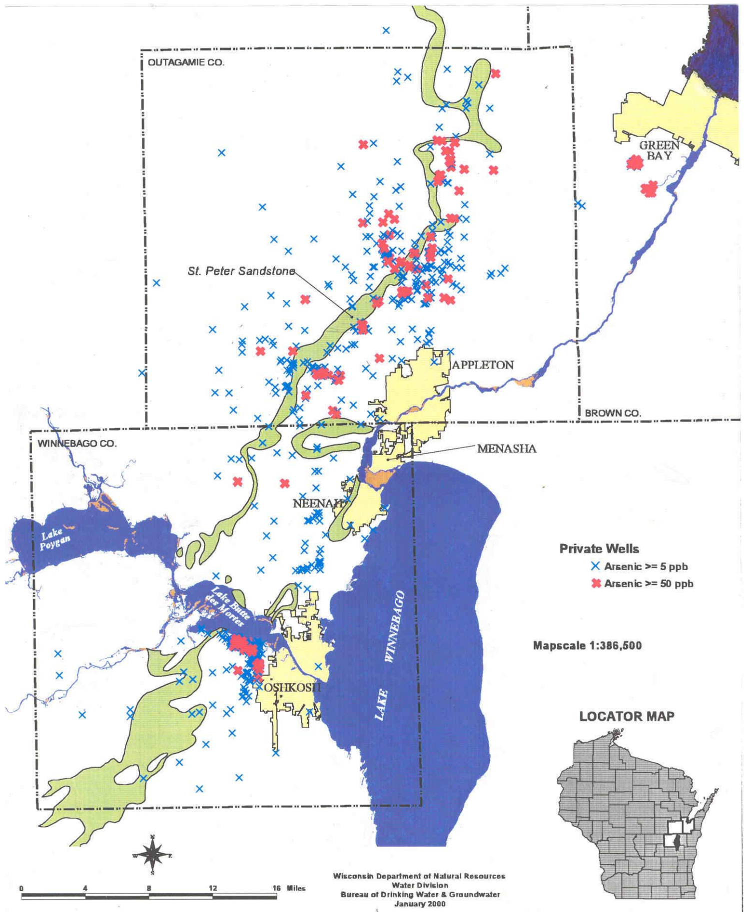

Figure 2. Arsenic-contaminated wells in northeastern Wisconsin. Small blue Xs indicate wells with arsenic contamination exceeding 5 ppb; large red Xs indicate wells with arsenic exceeding 50 ppb. (Map by Ann Achachte)

Causes of Arsenic Contamination

Results from several DNR studies indicate the geochemical phenomena causing the elevated concentrations of arsenic in the ground water of northeastern Wisconsin are associated with oxidation of sulfide-mineralized zones within most of the bedrock aquifers. The primary zone of mineralization extends some 10 feet below the base of the Platteville Dolomite, which is part of the main upper bedrock formation of this region. If the St. Peter sandstone is present within the geological sequence, it lies directly below the Platteville Dolomite and the arsenic-rich mineralized zone, then extends about 10 feet into this sandstone (Figure 3).

Geologists studying this problem think the minerals containing arsenic ere deposited within the bedrock aquifers of Wisconsin many millions of years ago. They theorize these minerals precipitated out of geothermal brines that migrated into Wisconsin in the Michigan Basin. Heavily laden with dissolved solids, these brines moved upslope through the permeable sedimentary bedrock layers that are common to Michigan and Wisconsin.

The geologic mechanisms that resulted in the arsenic contamination of the bedrock may have occurred in the following sequence: As sedimentary layers were being deposited in the enter of Michigan, one on top of the other, they accumulated into a thick layered sequence of bedrock, produced the Michigan Basin. The weight of all these layers at the center of the basin subjected the deepest layers to enormous heat and pressure. It converted the ground water in these formations to mineral-laden brines. It also caused these brines to be squeezed outward in all directions. In one direction, this ground water flowed westward, upslope through the bedding planes and fractures within the bedrock layers, and ended up in Wisconsin.

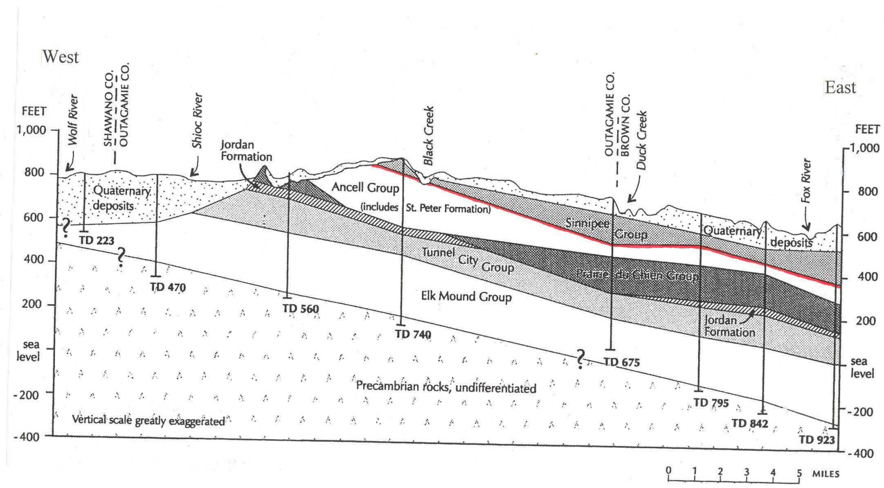

Figure 3. Geologic cross-section of northeastern Wisconsin. The primary zone of arsenic mineralization (sulfide-cement horizon) is designated by the red (dark) line just below the bottom of the Galena-Platteville Dolomite Formation (Sinnippe Group). (After W.G. Batten and K.R. Bardbury, Wisconsin Geological and Natural Hostory Servey)

These Michigan Basin brines contained a "suite" of heavy metals. As they advanced into Wisconsin, the minerals dissolved in them precipitated out and were deposited within the fractures and bedding planes of the bedrock. Here they remain today (Figure 4). The actual pathways of these mineral laden brines into the Wisconsin bedrock layers are not well understood. They could have first moved through the deeper sedimentary bedrock layers and flowed upward until they were stopped by the thin Glenwood Shale layer that lies at the base of the Platteville Dolomite. Alternatively, they may have flowed into Wisconsin within the shallower bedrock layers, where the minerals are concentrated today, and then moved downward into deeper layers.

It appears that oxidation of this sulfide-rich mineralized zone can initiate a complex set of geochemical reactions that can release arsenic into the ground water. Elevated levels of other chemical species, such as iron and other heavy metals, and the presence of very low pH water are often associated with high concentrations of arsenic.

Main Aquifer Resources

Recent analyses of sample results from some deeply cased replacement wells and a further examination of Wisconsin Geological Survey certified well logs seem to indicate that other arsenic-containing mineralized zones also exist much deeper, within the bedrock formations that underlie the Platteville Dolomite.

These include portions of the Cambrian Sandstone, the deepest sedimentary formation in this region. It is made up of a thick sequence of separate bedrock layers. As a whole, this bedrock sequence represents the primary drinking water aquifer of this region, especially for community and private high-capacity wells. This valuable sandstone aquifer extends all the way down to the pre-Cambrian basement bedrock. Thus, even deeply cased wells penetrating this deep aquifer are subject to some risk of contamination from arsenic.

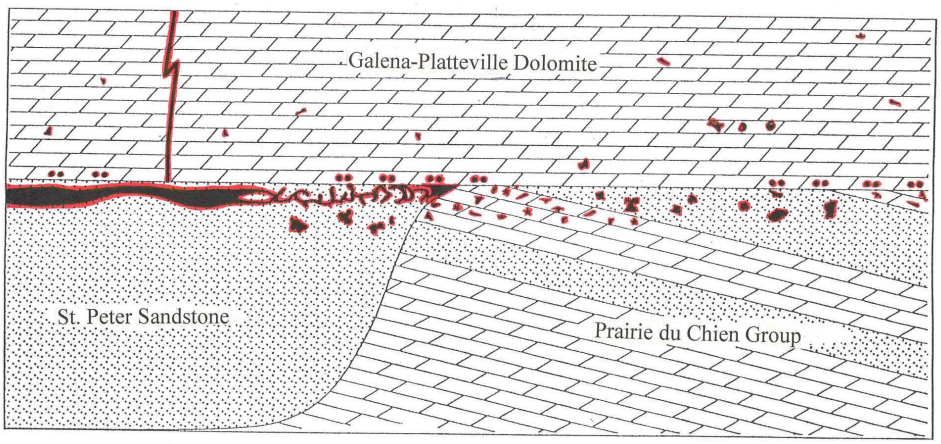

Figure 4. Configuration of the arsenic-laden sulfide-cement horizon, indicating its relationship to some of the sedimentary bedrock layers of northeastern Wisconsin. The St. Peter Sandstone was deposited on an erosional surface (unconformity), thus varies considerably in thickness and is entirely absent in some areas. (After J.A. Simo, PG. Freiburg, and K.S. Freiburg, University of Wisconsin-Madison Department of Geology)

The ancient crystalline pre-Cambrian bedrock is dense and unfractured and normally cannot provide sufficient volumes of water to a well. It therefore acts as a lower boundary to the bedrock aquifer system of this region and is not considered an aquifer. This basement bedrock is encountered at depths ranging anywhere from a few hundred to about 1000 feet below the ground surface in northeastern Wisconsin.

Health Effects of Arsenic Ingestion

Arsenic is an element that occurs naturally in the environment, both in organic and inorganic forms. The organic forms are essentially nontoxic. However, inorganic arsenic is very toxic and doses as small as 300 milligrams, an amount less than a teaspoon, can be lethal for an adult.

Drinking water with elevated concentrations of arsenic ingested over a period of years can increase the chances of developing a variety of health problems. These include noncancerous conditions such as anemia, diabetes, nerve and blood vessel damage, digestive problems, and skin lesions that involve changes in pigmentation and texture. In extreme cases, damage to the blood vessels can lead to gangrene of the lower extremities. The skin can become dark and develop into a condition known as "Black Foot Disease." This condition has been a problem in some areas of Taiwan.

Medical studies done throughout the world have shown that ingestion of arsenic can also cause an increased risk of several types of cancer, including skin, liver, bladder, kidney, and prostate cancer. Such arsenic-related health problems are prevalent in the country of Bangladesh and adjacent neighboring provinces of India. People who drink water contaminated with arsenic above a concentration of 50 ppb can have a risk of one in 1,000 of developing one of these cancers. Compared with other drinking water contaminants, this represents a high level of risk.

A study done in the southwestern coastal regions of Taiwan in the late 1960s and 1970s found an increased incidence of cancer in people who had consumed ground water with elevated concentrations of arsenic. Men of this region who ingested water with arsenic concentrations exceeding 600 ppb had a five fold increase in cancer rates, compared with the group of men whose water had arsenic concentrations below 300ppb. Women of this region also had an increased incidence of cancer, but at a rate less than half that of the men. However, the women who drank water with arsenic concentrations above 600 ppb had cancer rates 12 times higher than the women whose drinking water had concentrations below 300 ppb.

A 1993 study undertaken by Wisconsin’s Department of Health and Family Services evaluated the incidence of cancer among private well users in Winnebago and Outagamie counties. The researchers found an increased incidence of skin cancer among adults who had lived in their homes for more than one year and had elevated arsenic concentrations in their water. Skin cancer incidence was approximately three times higher among people whose drinking water had estimated arsenic concentrations exceeding 50 ppb.

Establishment of ’Arsenic Advisory Area’

Arsenic contamination of ground water was first identified in northeastern Wisconsin in 1987. It was one of the findings of a routine feasibility study for a landfill proposed to be located northwest of Oshkosh. As part of this study, drinking water wells in the vicinity of the proposed landfill were sampled for background inorganic chemicals. This was done to allow the DNR to establish baseline ground water quality for this area. In five of the eight wells tested, arsenic was detected above a concentration of 5 ppb. Sampling results from additional wells in the area surrounding this site indicated a similar trend of arsenic contamination. These results pointed toward naturally occurring deposits as the most likely source.

With further study in the early 1990s, DNR representatives were able to identify the regional extent of the arsenic contamination. They found the worst contamination to be within an area along a southwest to northeast trend, generally following the ground surface representation ("the subcrop") of the buried surface of the St. Peter Sandstone. For this area they developed special well construction specifications, more stringent than the minimum Private Well Code requirements. These specifications were recommended, but not required, for new wells constructed within an "Arsenic Advisory Area" designated by the DNR. This area includes a strip of land about 10 miles wide, extending five miles either side of the bedrock subcrop of the St. Peter Sandstone. It extends in a northeasterly trend, from a location just southwest of Oshkosh. to a location just west of Green Bay. The main zone of mineralization lies directly below the middle of this strip of land (Figure 5).

These more stringent specifications were designed to help ensure that new and replacement wells would be constructed to withdraw water from deeper portions of the bedrock aquifers, below the primary zone of mineralization. This increases the chances that water from new wells will have lower concentrations of arsenic. During the last decade, approximately 1,000 new wells have been constructed per year in this region. However, wells constructed to meet the DNR-recommended specifications usually cost several thousand dollars more than wells constructed to standard well code specifications. As a result, the vast majority of new wells do not get constructed to the more stringent specifications.

This fact alone may be contributing to the severity of the arsenic problem in this rapidly growing region. Ambient atmospheric air can readily move down into the open bedrock borehole of a typical shallow-cased well of this region. The oxygen in the air can come into contact with the mineralized zones within the bedrock and oxidize the minerals, thus triggering the geochemical reactions that release arsenic into ground water.

Most of the wells constructed to meet the more stringent construction specifications are producing water with arsenic concentrations below the current standard of 50 ppb. However, a small percentage of these wells have recently been showing signs of declining water quality, including rising concentrations of arsenic, iron, and low values of pH. Thus, even when new wells are constructed to meet the more stringent specifications, there is no certainty they will, in the long run, produce water low in arsenic. DNR researchers do not know if this is because of the existence of arsenic rich zones within the deeper bedrock formations, or because arsenic-laden ground water has moved downward from the primary mineralized zone.

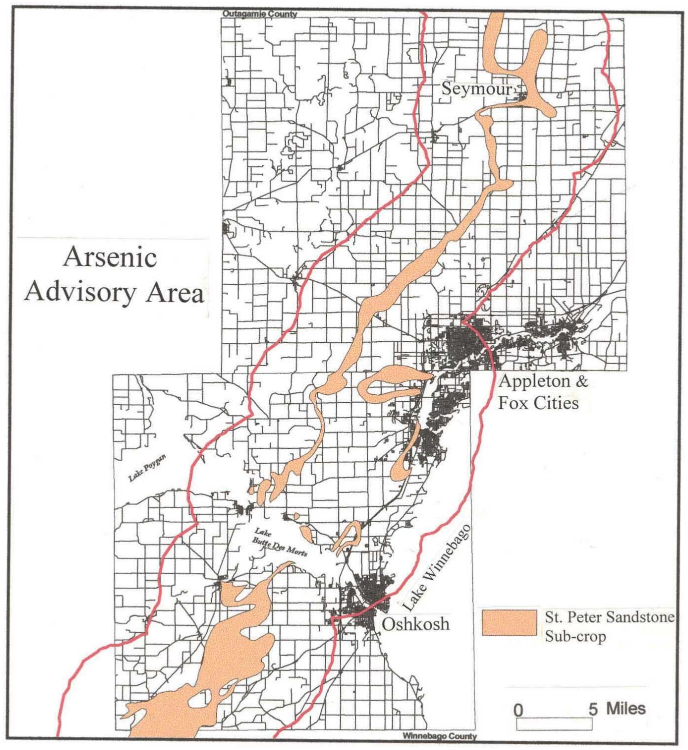

Figure 5. The "Arsenic Advisory Area" of northeastern Wisconsin. The two dark red lines, five miles either side of the sub-crop of the St. Peter Sandstone, bound this advisory area. (The city of Green Bay is just off the upper right comer of the map.) (Map by Rick Stoll)

Further information relating to the geochemistry of the arsenic problem came from a DNR investigation of a problem well in the Seymour area, just west of Green Bay. The owner had originally complained of declining water quality and reported that laundry washed in the well water literally fell apart. The DNR investigator noted that metal plumbing fixtures in the house showed evidence of significant corrosion. Water sample results indicated a very low pH, less than 2.5. The arsenic concentration of this water, 5,900 ppb, was very high. Elevated concentrations of other heavy metals were also present in the water. This was an extreme example of what appeared to be acid-type chemical reactions associated with the water quality problems of this region.

Additional sampling results demonstrated that several other wells in this area had similar water quality problems. Many of these wells also produced elevated levels of iron, sulfate and a suite of other heavy metals, including cobalt, molybdenum, vanadium, cadmium, chromium, copper, and nickel. This type of ground water contamination appeared to be affecting some of the bedrock aquifers in much of northeastern Wisconsin.

Well Replacements with State Grants

Funds from Wisconsin's Well Compensation Program have been used to replace some arsenic-contaminated wells in northeastern Wisconsin. Owners of existing wells can be eligible for these grants if the arsenic concentration of their water exceeds the present drinking water standard of 50 ppb. To date, DNR has funded the replacement of about 55 arsenic contaminated wells.

Based on initial sample results following well completion, all but one of these wells were successful in providing water with an arsenic concentration below the 50 ppb standard. However, recent follow-up sample results indicate that five of these replacement wells, initially successful, are now producing water with arsenic concentrations exceeding the drinking water standard. Some of these wells have concentrations above 1,000 ppb.

The results of these five unsuccessful wells have caused DNR representatives to question whether their construction specifications for replacement wells are stringent enough to ensure these wells will withdraw water from below the arsenic-contaminated zones within the bedrock aquifers. The construction specifications for the well compensation replacement wells usually require grouted casing to extend to a depth at least 80 feet below the primary zone of mineralization. These specifications are also recommended for other new and replacement private wells constructed within the arsenic advisory area.

Associated Contributing Problems

A general review of water sample results collected in the last two decades indicates a trend of increasing numbers of wells that produce water with at least a detect of arsenic. This includes new and existing wells. More important, the concentration of arsenic in these wells also appears to be increasing with time.

Since the 1950s, many thousands of new private wells have been constructed in northeastern Wisconsin. The use of these wells, along with increased use of both municipal and industrial wells in this region, has caused ground water consumption to rise. This rise is due to a growth in population and an increase in the per capita consumption of water. As a result, regional ground water levels in the sedimentary bedrock aquifers of northeastern Wisconsin have shown a steady long-term decline. The decline has averaged as much as 3 to 4 feet per year in the Green Bay area and as much as 2 to 3 feet per year in the Fox Cities area surrounding the city of Appleton.

These declines also seem to be having an adverse impact on the arsenic problems of this region. In many areas, increasing concentrations of arsenic may be a result of the water table dropping to levels at or just below the main layer of mineralization and then fluctuating up and down across this layer. This fluctuation can allow oxygen in the air to come in contact with and oxidize the sulfide minerals in this layer containing the arsenic. This initial oxidation can then trigger the geochemical reactions that can eventually release the arsenic into the ground water. It appears that, once triggered, these reactions are self-sustaining and can thereby continue to release arsenic.

A percentage of the wells with high concentrations of arsenic also have high levels of iron. Iron concentrations in a few of these wells have been in the hundreds of parts per million. It appears that a significant portion of the arsenic may be held and subsequently released out of the iron compounds. This is likely because arsenic is associated with the iron sulfide minerals pyrite, marcasite, and arsenopyrite. When oxidized, these minerals can weather into minerals such as melanterite and other iron oxyhydroxides. Melanterite is light in color, soft, flaky, and soluble. When dissolved in ground water, it can release both arsenic and iron compounds into the water.

Special Well Construction Methods

DNR representatives are also concerned that the use of air-rotary well drilling methods may be contributing to the arsenic problems of this region. Oxygen in the volumes of compressed air that flow through mineralized horizons of the bedrock during construction of wells may also be triggering these geochemical reactions. Because of this concern, the DNR has formulated alternate drilling method guidelines for wells constructed within the arsenic advisory area. When well drillers follow these guidelines, they can help reduce the risk that the well construction process will trigger these reactions.

The special construction specifications are presently in draft status and are therefore subject to change. DNR representatives are not sure if it will be appropriate to limit the use of air-rotary methods for the construction of wells in this region. One of the main alternative construction methods, rotary-mud circulation, is also not risk-free in this regard.

Other alternative construction methods are also being evaluated. These include the use of rotary water circulation, dual-rotary, and dual-wall, air-reverse rotary methods. The dual-rotary method can allow an outer casing to be "turned" into formations, perhaps beyond mineralized layers, and then retracted during or following the grouting process. The dual-wall, air-reverse rotary method allows the use of compressed air to "draw" the drill cuttings up through the center of the drill stem. This might help prevent the compressed air from coming in contact with the mineralized zones during the drilling process.

However, some well drillers have pointed out that all of these alternative methods have some practical problems. For example, when using only water as the drilling fluid, it can be difficult to raise the drill cuttings up and out of the hole. This problem can increase the risk of the drill string becoming stuck in the hole as drill cuttings fall back down toward the bit. Dual-rotary drilling rigs have traditionally been more expensive than other options, although smaller, less expensive models are now available. Most drillers are not equipped with the type of dual-wall drill stem that is necessary for use of the air, reverse-rotary methods, and it is expensive to equip a rotary drilling machine for this method. These conditions present economic problems for well drillers.

Strategies for Addressing the Arsenic Problem

Due to some of these recent findings, and because of unresolved drilling method and construction specification issues, DNR representatives have recognized the need to further study this problem. It's important to them to try to more fully understand the water quality problems of this region and the mechanisms that are releasing arsenic into the ground water before they try to develop solutions to these problems. For this purpose, they have established a statewide work group of professionals who have expertise in various fields that relate to this problem.

This group has been assigned to study the arsenic problem in greater depth, to develop strategies to manage the arsenic contamination, and to try to alleviate its potentially adverse health effects. Mike Lemcke, Chief of Wisconsin's Groundwater Section, has been placed in charge of this work group. The group includes members from the DNR's Drinking Water and Ground Water Program, representatives from other state agencies, the U.S. and Wisconsin Geological Surveys, several Wisconsin universities and their extensions, local county health departments, the National Institute of Health, and the Wisconsin Water Well Association.

More specifically, this group has been assigned the responsibility of addressing the following issues:

- The need to more clearly define the geographical and vertical extent of the arsenic contamination, along with the presence of associated heavy metals and other related water quality problems within the regional and statewide aquifer systems.

- The need to understand the geochemistry and flow regime of the ground water systems, especially to determine what may trigger and sustain the geochemical reactions that release arsenic and other metals into the ground water, and to determine the mobility of these contaminants within the ground water systems.

- The need to develop possible solutions to the arsenic, and other associated heavy metal, contamination problems of Wisconsin. These solutions may include more stringent and alternative well construction methods and specifications, the possible need for the installation of "cluster wells" or community water systems, and the available options for water treatment technology and equipment.

- The need to re-examine available toxicology and risk assessment studies to more clearly determine possible future impacts to human health and the ground water resources of this region.

- The need to develop information and education strategies to help the work group clearly communicate the nature of these problems to the public.

We hope this group will be successful in finding practical, long-term solutions to these problems that are within the economic means of private well owners and public water utilities.

Tom Riewe is a hydrogeologist with the Private Water Systems Section of the Bureau of Drinking Water and Groundwater, Department of Natural Resources, Madison, Wisconsin.

Annette Weissbach (at the time of the initial arsenic research) was a hydrogeologist with the Environmental Repair Program of the Northeast Region of the Department of Natural Resources, Green Bay, Wisconsin.

Liz Heinen is a drinking water system specialist with the Private Water Systems Program of the Northeast Region of the Department of Natural Resources, Mishicot, Wisconsin,

Rick Stoll is a hydrogeologist with the Northeast Region of the Department of Natural Resources, Green Bay, Wisconsin